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ACTION OF TETRAZO DITOLYL CHLORIDE AND TETRAZO DIPHENYL CHLORIDE ON CERTAIN ALCOHOLS.

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A Dissertation submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy

by

James Henry Curry Winston.

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Baltimore, Maryland,
June, 1899.

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Acknowledgement.

The following investigation was taken up at the suggestion of Professor Ira Remsen and was carried on under his personal supervision and guidance in the chemical laboratory of the Johns Hopkins University during the scholastic year 1898-1899. I hereby desire to express my deep indebtedness to him for his invaluable assistance and thank him for his uniform kindness and constant encouragement during my connection with this university.

I also wish to express my obligations to Professors H. N. Morse and Edward Renouf in Chemistry, Professor Joseph S. Ames in Physics and Doctors L. S. Hulburt and A. Cohen in Mathematics for instruction and advice.

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Introduction.

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For a number of years investigations have been carried on in this laboratory under the personal guidance of Professor Ira Remsen having as their object the determination of the conditions which influence the character of the reaction between diazo compounds and alcohols.

In this field investigations have been carried on by Broun(1), Palmer(2), Orndorff(3), Graham(4), Dashiell(5), Metcalf(6), Parks(7), Shober, Beesen(9), Weida(10), Chamberlain(12), Bromwell(13), Cameron(14), Moale(15, and Franklin(16).

These investigations have shown that the reaction is affected by many things, among which are the nature and position of the substituting group in the diazo compounds, the alcohol employed, the temperature and pressure under which the reaction takes place, presence of water, of alkalis, and of finely divided metals. The number of cases thus far studied is, however, comparatively small and it is impossible at present to formulate a law or draw generalizations

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(1) Am.Chem.Jour. 4-374. (2) Ibid. 8-243. (3) Ibid. 9-387. (4) Ibid. 11-319. (5) Ibid. 15-124. (6) Ibid. 15-301. (7) Ibid. 15-320. (8) Ibid. 15-379. (9) Ibid. 16-235. (10) Diss. 1894. (11) Am.Chem.Jour.19-163. (12)Ibid 19-531. (13) Ibid.19-563. (14) Ibid.20-229. (15) Ibid. 20-298. (16).Ibid. 20-458.

by which one can predict ~~tell beforehand~~ in what way any diazo compound will decompose with an alcohol under given conditions.

It was this uncertainty and the desire on the part of Dr. Remsen to add another link to the chain, that led him to suggest to me the study of the decompositions of the diazo compounds obtained from the hydrochloric acid salts of *p*.diamido.*m*.ditolyl (*o*.tolidine) and *p*.diamido-diphenyl (*p*.benzidine) with the alcohols.

The results of this work are recorded in the following pages which are divided into an experimental and general part - the former a simple record of the work actually done - the latter, historical, and showing the relation of this work to that which has preceded it.

I.- EXPERIMENTAL PART.

A. Tetrazo-ditolyl Chloride.

PREPARATION OF TOLIDINE HYDROCHLORIDE. - One hundred grams of tolidine were placed in a two-liter evaporating dish and one liter of water added. The mixture was heated up and hydrochloric acid added in considerable excess when the hydrochloride was formed and went into a clear red solution. This solution resulting was decolorized by boiling a few minutes

with animal charcoal. The clear solution is now filtered off hot and yields the hydrochloride on cooling in crystalline form. It was found best to get the rest of the hydrochloride from the solution by adding concentrated hydrochloric acid till no more of the hydrochloride was precipitated, since, on boiling the solution to reduce its volume and induce another crystallization, not only did the solution become strongly colored, but also some of the tolidine was precipitated as the mono-hydrochloride. The salt when precipitated differs not materially in purity from that obtained by crystallization, and fractional crystallization gave products differing from each other very little in this respect. The hydrochloride obtained by this method was perfectly white. For working purposes it was found best to make the hydrochloride entirely by precipitation with hydrochloric acid as it was then obtained in very small, fine crystals with which the nitrous acid readily and completely reacted.

It was also found that a better quality of the diazo compound was obtained by using the hydrochloride as soon as filtered, when it was still moist, and this was afterwards shown to be due to the hydrochloric acid present, as the same result was reached by adding a few drops of the acid when the dry hydrochloride was used. The hydrochloride if allow-

ed to remain in contact with the air gradually becomes colored purple on the surface, but if it is previously washed with concentrated hydrochloric acid this power of becoming colored in the air seems to be almost entirely lost.

PREPARATION OF TETRAZO-DITOLYL CHLORIDE.-

The method that was found to work best was the usual one of passing the oxides of nitrogen, formed by the action of nitric acid on arsenious oxide, into a thin paste of the tolidine hydrochloride and water. The gases are passed from the flask in which they are formed through a Wolff's bottle placed in cold water to condense any water or nitric acid that might distil over. In case the hydrochloride was obtained by crystallization, it was ground very fine in a mortar, and it was found advisable to grind it with a little water, as, when reduced to a powder, it fills the atmosphere, attacking the mucous membrane of the nose and throat. Its marked power to produce sneezing was clearly evidenced. The relative proportions of water and hydrochloride that were found best were about three parts of water to one of the salt. It is best to add the hydrochloride from time to time as the solution clears up, beginning with about half of the amount to be used. This is necessary because there is formed some in-

termediate product which stiffens up the paste to such an extent that in case the whole amount of the salt is used at first, diazotization becomes almost impossible. The proportions of 3 to 1 are about those which will give a complete solution of the diazo-compound in water. The diazotization was carried on in cylinders which were placed in a vessel containing water in which pieces of ice were kept floating. When the diazotization begins, the mixture assumes a greenish color which rapidly changes to a dark purple, and it is at this stage that the amount of solid matter present seems to be greatest. When the diazotization approaches completion the solid goes in solution, and this quickly clears up to a light straw color. This is then poured into about ten times its volume of ordinary 95% alcohol which has been previously cooled in a freezing-mixture of salt and ice. The diazo compound at once is precipitated as a flocculent, yellow substance. The vessel containing the diazo mixture is allowed to remain for some time in the freezing-mixture, and the tetrazo-ditolyl chloride is then filtered off, ~~and~~ washed with alcohol and ether, and then spread on drying-paper and allowed to dry. For filtering it a Büchner funnel was found to be of the greatest service as a time and labor saver. The yield of the diazo compound by this method is about 80% of the theoretical amount. The disposition of the mother-liq-

uor from the precipitation will be spoken of later. Many methods were tried in the hope of obtaining the diazo compound crystalline, ~~and~~ but such a result was never reached, and the method described was found to be the best.

Action of tetrazoditolyl chloride on absolute methyl alcohol. -

10 grams of the diazo compound were introduced into a half-liter flask and 200 c.c. of absolute methyl alcohol added. No change was noticeable at room temperature. The flask, attached to a reflux condenser was placed on a water-bath and gently heated. The decomposition began only when the temperature reached almost that of the boiling point of the alcohol, and then proceeded smoothly with the copious evolution of nitrogen until the reaction was completed and a perfect solution resulted. This required about half an hour. The solution was then boiled for a few moments to insure complete decomposition. During the whole operation no odor of aldehyde was perceptible. As the operation proceeded the alcoholic solution changed color, gradually darkening, until at the end it was of a dark red color. On allowing the solution to cool, crystals in the form of reddish leaves separated, which were filtered off. Almost half of the alcohol was then distilled, and on cooling a very small crop of crys-

tals resulted. All of the alcohol was then removed from the flask by distillation and was of a slightly yellow color. The methyl alcohol thus obtained was poured into a beaker and six volumes of a saturated solution of sodium chloride added but no oil separated. The color of the alcohol was probably due to particles of the tarry residue mechanically carried over during the process of distillation. The tarry oil remaining in the distillation flask was easily soluble in ordinary alcohol, but from it nothing of value was ever obtained. Purification was attempted by means of animal charcoal, but the red color could not be thereby removed. On partial evaporation nothing was obtained by crystallization, and on completely evaporating the alcohol the same unpromising oil resulted. Some of this was allowed to stand for weeks in the hope that something would crystallize out. Solidification by means of a freezing-mixture was attempted but it remained always the same tarry oil. Some of it was put in a distillation bulb and subjected to distillation. The residue remaining in the bulb after the last traces of alcohol and water were removed, solidified to a black cake but was non-crystalline, and from it nothing could be gotten. It was thought that, if there was any of the hydrocarbon corresponding to this tolidine which is known to be an oil, formed in the decomposition of the diazo compound, ~~that~~ it

could be separated from the tar by distillation with water vapor. So to the flask containing the tar was added a little water and then steam passed through the flask but no oil was carried over with the water vapor. So it was decided to give up this search and seek more fruitful fields. The crystals which had been obtained by the action of methyl alcohol on tetrazoditolyl chloride were dissolved in ordinary alcohol, the solution decolorized with animal charcoal, and from this on allowing a hot concentrated solution to cool, was obtained the substance in the form of beautiful, almost colorless leaves. These were recrystallized from alcohol until the melting-point became constant and were obtained as silvery leaves which had a sharp melting point of 145.5° C. This substance is insoluble in water very sparingly soluble in cold alcohol and ether, rather soluble in boiling alcohol. The difference in solubility in alcohol at its boiling-point, and a few degrees below was very marked. Two analyses gave the following results:

(1) 0.2000gm. substance gave 0.1337gm. H_2O, 0.5801gm. CO_2.

(2) 0.2000gm. substance gave 0.1336gm. H_2O, 0.5812gm. CO_2.

The calculated percentages of the elements for demethoxy-m-ditolyl, $C_{14}H_{12}(OCH_3)_2$ are -

C - 79.34% , H - 7.44% , O - 13.22%

	calculated	found (1)	found (2)
C	79.34	79.10	79.11
H	7.44	7.43	7.43
O	13.22	13.47	13.46

The compound analysed is, therefore, dimethoxy-m-ditolyl, $C_{14}H_{12}(OCH_3)_2$. There are two ways in which the reaction between tetrazoditolyl chloride and methyl alcohol might take place; first is the one in which in the diazo-compound, the diazo group is replaced by hydrogen, or the so-called "hydrogen reaction" or, secondly, the methoxy residue of the methyl alcohol might replace the diazo group or the so-called "alkoxy" reaction." These two reactions are expressed in the following equations:

(1) $C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{14} + 2CH_2O + 2N_2 + 2HCl$

(2) $C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{12}(OCH_3)_2 + 2N_2 + 2HCl$

It is observed that, in the case of the substances brought together in the decomposition described above and under the conditions indicated, the reaction takes place in accordance with the second equation and indeed the most careful search fails to reveal any evidence that the first

reaction takes place at all, when this diazo compound is treated with methyl alcohol under the conditions names. It was considered advisable to vary the conditions of the reaction to discover how the decomposition is best effected, and also to study the effects of variations in temperature and dilution of the alcohol as well as the presence of certain substances known to affect the reaction.

Decomposition of the diazo compound at room temperature.- About 15 grams of the diazo compound were placed in a half-liter flask and 250 c.c. of absolute methyl alcohol added and the mixture was allowed to stand at room temperature for two weeks,alcohol being added from time to time to make up for evaporation. By the end of this time most of the diazo compound had gone in solution,and the alcohol had acquired a dark red color,but at no time was an evolution of nitrogen noticeable,neither was the odor of aldehyde perceptible. At the end of this length of time the flask was attached to a return conductor and the alcohol boiled on a water-bath,when nitrogen was evolved freely, and the reaction was complete in half an hour. The yield of the crude ether was a little over 4 grams but was not as pure as that made from the decomposition of the freshly made diazo compound. All efforts made to obtain the hydrocarbon from the alcohol which was distilled off as well as from the res-

idue in the distillation flask were as futile as those in the previous experiment.

Decomposition of the diazo compound at the boiling temperature of methyl alcohol.-

Fifteen grams of the same diazo compound were decomposed with absolute methyl alcohol at the boiling temperature of the alcohol. The decomposition was completed in half an hour, the evolution of nitrogen being rapid, and the solution turning red as before. Almost 4 grams of the ether were obtained which was not as deeply colored as that obtained in the preceding experiment. As before, no other product was isolated, and it seems that no other reaction than the "methoxy" one takes place in this decomposition. It was next thought best to see what effect a dilution of the alcohol with water would have.

Decomposition of the diazo compound with dilute methyl alcohol -

23 grams of the diazo compound were decomposed with methyl alcohol diluted with 5% of its volume of water. This was accomplished in the usual manner by heating the mixture to the boiling-point of the alcohol when the decomposition proceeded smoothly and quickly. On cooling there was obtained a weight of the ether of a little over five grams.

The reaction was not as clean as in the cases in which the absolute alcohol was used, the solution being more deeply colored, and the product more impure. 18 grams of the diazo compound were decomposed with methyl alcohol diluted with 10% of its volume of water, and the decomposition effected exactly as before. The results were in every way similar. The yield was 4 1/2 grams of the ether. After this many other similar experiments were carried on. The water solution of the diazo compound, after the diazotization was completed was added to ten times its volume of methyl alcohol and the diazo compound decomposed in the usual way. The percentage of the ether obtained was in every case nearly the same. When, however, the percentage of the water was as high as 40% to 50%, then the yield of the ether was materially diminished, and the amount of tarry products relatively greater. In all cases of dilution the product was not as pure as in those cases in which the absolute alcohol was used, so that although the yield was not materially better when the absolute alcohol was used than in those cases in which the alcohol was diluted to within 20% of its volume with water, yet the absolute alcohol method was finally adopted to the exclusion of the others, as the alcohol was ready for another decomposition as soon as distilled off, and the reaction by

this method was cleaner in every way. I decomposed in this way 180 grams of the diazo compound, from which was obtained a yield of 42 grams of the crude ether which when purified gave 33 grams of the pure dimethoxy-m.ditolyl. I will describe in detail one experiment in which the weighings were very carefully made, and in which the decomposition was effected in the manner that was found best. 60 grams of tolidine hydrochloride was ground very fine in a mortar with water. Half of this was put in a cylinder and 150c.c. of water added (the whole amount of water used was 190c.c.). This was cooled in a bath in which was water containing pieces of ice. A rapid current of the oxides of nitrogen was then passed into the mixture, and the rest of the hydrochloride added in portions as the solution began to clear up. At the expiration of half an hour the diazotization was completed and a clear yellow solution of the diazo salt in water resulted. This was poured with stirring into two liters of ordinary alcohol which had been previously cooled in a freezing-mixture. The diazo compound was at once precipitated as a flocculent yellow substance. In half an hour this was filtered off, washed with absolute alcohol and ether, and allowed to dry on drying paper. 43 grams of tetrazo-ditolyl chloride were thus obtained. This was placed in a flask

having a capacity of one liter and a half, and 500c.c. of absolute methyl alcohol added. The flask attached to a reflux condenser was put on a water-bath, and the mixture heated to the boiling point of the alcohol for half an hour when the decomposition was complete. There were obtained 11.5 grams or 34% of the theoretical yield of dimethoxy-m-ditolyl, which when purified gave 9.8 grams, or 29% of the theoretical amount of the pure substance. The disposition of the alcoholic filtrate from the precipitation of the diazo compound will be spoken of when the preparation of dimethoxy-m-ditolyl is taken up.

Decomposition of tetrazo-m-ditolyl chloride with ethyl alcohol.-

20 grams of the diazo compound were placed in a half liter flask and 200c.c., of absolute ethyl alcohol was added, and the diazo compound decomposed at the boiling temperature of the alcohol. Throughout the operation aldehyde was given off and easily recognized by its odor, and, after the reaction was completed, the alcohol smelled strongly of it. On allowing the alcoholic solution to cool, crystals were obtained which resembled those obtained by the decomposition of the diazo salt with methyl alcohol. From 20 grams of the diazo compound 2 1/4 grams of the crude product were obtain-

ed. The alcohol was then distilled off and six times its volume of a saturated solution of sodium chloride was added but nothing was obtained in this way. The tarry oil in the distillation flask was then subjected to distillation in steam, and a few drops of a yellow oil were obtained. From the tar remaining in the flask nothing further was ever gotten. These experiments were repeated many times, and the yields were relatively about the same in every case. The amount of the oil formed was never determined accurately because it was volatile with difficulty with steam, but appeared to be formed in nearly the same amount as the crystalline solid. In water the oil sometimes remained at the top, sometimes sunk to the bottom and often remained suspended throughout the liquid showing its density to be about the same as that of the water. After a sufficient amount of it had been obtained, it was taken up from the water with ether, dried, and subjected to distillation. It passed over almost wholly at 280°- 281° and was recognized as m-ditolyl which has a specific gravity of 0.9993 at 16°. This substance was discovered by Schultz (1) in 1884, who obtained it as one of the products of the action of nitrous acid on an alcoholic solution of o-tolidine. He describes it as a yellow oil boiling at 281°, which by oxidation with potassium bichromate and sulphuric acid yields isophthalic acid. By careful ox-

idation in acetic acid solution with the calculated amount of chromic acid he obtained a new acid, diphenyl di-m-carboxylic acid melting at 193°. In 1888, Stolle(1) repeated Schultz's work and made many derivatives of this hydrocarbon. He gave as its boiling point 289°. A short while afterwards Perrier(3) succeeded in oxidizing one of the methyl groups by means of nitric acid (s .gr.1.14), and obtained the mono-carboxylic acid of m-ditolyl. The crystalline solid which had been obtained in these decompositions was dissolved in alcohol, and decolorized with animal charcoal. It is not as soluble in alcohol as is the product obtained from the decomposition with methyl alcohol, and the difference in solubility at the boiling temperature of alcohol and a few degrees below is even more marked than is this difference with di-methoxy-m-ditolyl. It is insoluble in water and practically insoluble in cold alcohol and ether.

On cooling of the alcoholic solution, it crystallizes in beautiful pearly plates melting sharply at 154°. This compound was therefore supposed to be di-ethoxy-m-ditolyl, first obtained by Schultz, by the action of nitrous acid on an alcoholic solution of o.tolidine. He gives the melting point as 156°. About two years later the same substance was made

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(1) Ber.d.Chem.Ges. 17-468.
(2) Ber.d.Chem. Ges. 21-1096.
(3) C.R., 114-484.

by Hobbs by treatment of the potassium salt of di-hydroxy-*m*-ditolyl with ethyl iodide. In order to become perfectly certain of the identity of this compound it was analysed. Diethoxy-*m*-ditolyl is composed of C - 80.00% H - 8.1% and O - 11.9% . The results of three analyses follow:

(1) 0.2000gm. substance gave 0.145gm. H_2O and 0.5885gm. CO_2.

(2) 0.2000gm. substance gave 0.1451gm. H_2O and 0.5916gm. CO_2.

(3) 0.2000gm. substance gave 0.1444gm. H_2O and 0.5886gm. CO_2.

	calculated.	found. (1)	(2)	(3)
C	80.0	80.25	80.70	80.30
H	8.1	8.05	8.10	8.00
O	11.9	11.70	11.30	11.70

Thus it is seen that when tetrazo-*m*-ditolyl chloride is decomposed with methyl alcohol, the "alkoxy reaction" only takes place, while, ~~in the instance in which~~ when the decomposition of the diazo compound is effected with ethyl alcohol, both the "hydrogen" and the "alk oxy" reaction takes place. The reaction with ethyl alcohol is not as clean as that in which methyl alcohol is used, neither are the products formed in as large amount except those of a tarry nature which are relatively greater.

¶ *Decompositions of the diazo compound with ethyl alcohol under varying conditions of temperature and dilution of the alcohol.*

Some of the diazo compound was allowed to stand in contact with absolute ethyl alcohol for two weeks. The odor of aldehyde was noticeable at any time if the mixture was shaken up, but at the end of this time the greater part of the diazo compound was still undecomposed, although much of it had undergone some change as was ~~evidenced~~ shown by the deep-red color of the solution. The flask containing the partially decomposed diazo compound was attached to a reflux condenser, and the alcohol heated to its boiling-point, when nitrogen was freely evolved, and the decomposition completed. The diethoxy-m-ditolyl and m-ditolyl were separated as before, and their relative amounts were the same as found before. The decomposition was effected with ordinary 95% alcohol by the usual method of heating to the boiling-point of the alcohol. The yields were the same as before. Many experiments were carried on with varying dilutions, as the result of which it was found that the relative amounts of the oil and crystallised solid were not materially affected by diluting the alcohol up to 20% of ~~that~~ its volume with water, and also the total yields were about the same. The resulting solution in these cases was of a dark red color and the reaction seems to be as clean as when absolute ethyl alcohol is used. When the alcohol is diluted with more than 20% of its volume of water the yields of m-ditolyl and diethoxy-m-

ditolyl diminish, and with increasing dilution the reaction is less clean and the amount of tar formed greater. Most of the diethoxy-*m*-ditolyl used in this investigation was made as a by-product in the preparation of dimethoxy-*m*-ditolyl. The alcohol-water mixture from which most of the diazo compound had precipitated was poured into a flask of convenient size, and the remaining diazo compound decomposed by heating the solution on a water-bath. Half of the alcohol was then distilled off, and when the solution ~~is~~ was allowed to cool the diethoxy-*m*-ditolyl crystallized out. The *m*-ditolyl was not separated from the residue in the flask because of the difficulties attending such an operation, and more especially because another method of preparing this was discovered by which it could be obtained in any desired amount and in almost quantitative yield. It was thought that the products resulting from the action of nitric acid on these phenol-ethers would prove of interest so our attention was next turned to them.

Action of nitric acid on dimethoxy-*m*-ditolyl.-

In a test-tube some of this ether was put and dilute nitric acid added. The action was very slow even on boiling the acid, while at ordinary temperature there was no action at all. The same experiment was tried with concentrated nitric acid, and on heating the mixture slightly the reaction

proceeded smoothly, until all the ether had gone into a red solution. On the addition of water quite a voluminous yellow precipitation resulted. Some of the di-methoxy-*m*-ditolyl was treated with fuming nitric acid. The reaction was very violent, the acid consuming the ether greedily, and much heat was generated by the reaction. On the addition of water some of the yellow precipitate was thrown down but the yield was not nearly as good as that from the previous experiment, as the fuming nitric acid oxidized a large part of the ether. The action with concentrated nitric acid was found to give the best results so this method was used in the preparation of the nitro-compound. 10 grams of di-methoxy-*m*-ditolyl were thus treated in small portions with concentrated nitric acid. At first the action was energetic, heat being evolved. When this first action was over, the mixture was heated until the reaction was complete, and all of the ether had gone into solution. When water was added, the nitro product precipitated as a pasty mass, which harden~~s~~ed when shaken with water. This was filtered, washed with water, and after drying was dissolved in alcohol in which it is very soluble, decolorized with animal charcoal and recrystallized from alcohol until a constant melting-point was reached. When a cold alcoholic solution not quite concentrated ~~were~~ was allowed to stand until the product crystallized out, it was obtained in straw-colored

rhombs, but, on allowing a hot concentrated solution to cool, the nitro-product was obtained in beautiful straw-colored needles. The melting-point of both was the same, that is, 130.5°. Three determinations of nitrogen according to the absolute method gave as its percentage therein 13.5%, 13.24% 13.4%, which makes it probable that, by the action of concentrated nitric acid on di-meth-oxy-m.ditolyl, we get tetra-nitro-di-meth-oxy-m.ditolyl for which the formula is -

$C_{14}H_{12}O_2(NO_2)_4$. It was desired to obtain enough of this to convert it into its amido derivative and study that compound, but enough of the tetra-nitro product was not obtained, and this special line of work was given up for the present. The yield of the tetra-nitro-dimeth-oxy-m.ditolyl from ~~the~~ ten grams of dimeth-oxy m.ditolyl was 4 1/2 grams of the purified substance.

Action of nitric acid on diethoxy-m.ditolyl.-

It was found by treating small portions of the ether in a test-tube with dilute, concentrated, and fuming nitric acid, that the best yield of the nitro product was obtained by the action of fuming nitric acid without any heat but that generated by the reaction. When concentrated nitric acid was used as was found best in the case of the nitration of dimethoxy-m.ditolyl, it was necessary for a com-

plete reaction to heat the nitric acid to its boiling-point for quite a while, in which case most of the ether was oxidized and little of the nitro-product obtained. Five grams of diethoxy-*m*-ditolyl were treated in a large test-tube with fuming nitric acid until it went into solution. The change was accompanied with the evolution of heat and was completed in from two to three minutes. Water was then added until no more of the nitro-compound ~~would~~ was precipitated on further addition. The precipitate was then filtered, washed, dried, dissolved in alcohol, decolorized with animal charcoal, and recrystallized from alcohol until the melting-point became constant and sharp. This substance is very soluble in alcohol, from which it crystallizes as in the case of tetra-nitro-dimethoxy-*m*-ditolyl in rhombs or needles depending on conditions. The substance is of a straw color, and the needles resemble dinitro-benzene very much. The melting-point of this substance is 142°. The compound was analyzed by a determination of its nitrogen. Three analyses gave 12.9%, 12.5% and 12.6% as the percentage of nitrogen contained, which corresponds to the formula $C_{18}H_{18}O_2(NO_2)_4$, tetra-nitro-diethoxy-*m*-ditolyl in which the percentage of nitrogen is 12.45%.

PREPARATION OF DIHYDROXY-M.DITOLYL OR O.DICRESOL.-

In 1888 Gerber(1) and Hobbs(2) prepared this substance by boiling a water solution of tetrazo-m.ditolyl chloride, and obtained it in the form of large, broad needles, melting at 157°. It was thought well to repeat these experiments. It was found that unless the solution was very dilute very little of the o.dicresol was formed, and that a few drops of sulphuric acid increased the yield of that substance. I will describe an experiment in which the proportions were such as to give the best yield of the o.dicresol. Ten grams of tolidine hydrochloride were diazotized in the usual manner. The water solution of the diazo-compound was poured into a three liter flask and 1800c.c. of water added. After the addition of a few drops of sulphuric acid the whole was boiled for fifteen minutes. On cooling, the tar formed became attached to the sides of the flask, and from the clear solution the o.dicresol was obtained in the form of large broad needles. The yield was 2 1/2 grams. The crystals were further purified by crystallization from boiling water, and melted sharply at 155°. O.dicresol is very soluble in alcohol, and remains in solution as long as any alcohol remains. When the alcohol has all evaporated the o.dicresol is obtained as plates, always of a brown color. A water-al-

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(1) Ber. d. Chem. Ges. 21-749

(2) Ber. d. Chem. Ges. 21-1065.

cohol mixture was found to be an excellent solvent for the *o*-dicresol, from which it crystallized perfectly white in needles. It was thought that it would be interesting to attempt the preparation of *o*-dicresol by Graebe's method for the preparation of phenols by the action of the halogen acids on phenol ethers in sealed tubes at high temperatures. 5 grams of dimethoxy-*m*-ditolyl were mixed with 10c.c. of concentrated hydrochloric acid, and the mixture put in a glass tube which was sealed up and heated to 225° for three hours. When the tube was cold, it was opened and the contents removed. The solid which was filtered off was black from the separation of carbon ~~evidencing~~ showing too high heating. None of the dimethoxy-*m*-ditolyl remained unchanged, but a substance resulted, very soluble in alcohol and ether, soluble in boiling water from which on cooling it crystallized in large, broad needles, which, when purified ~~and recrystallized~~, melted at 156°. The melting-point, solubility in different solvents, and form of crystals made it so probable that the substance formed was *o*-dicresol that analysis was considered unnecessary.

10 grams of the same ether together with 20c.c. of concentrated hydrochloric acid were put in a tube which was sealed and heated to 200° for 5 hours. There was very little separation of carbon and the reaction was complete. 3 1/2 grams of the purified *o*-dicresol were obtained, the crystals

melting at 155°.

Action of sodium methylate on the diazo-compound.-

20 grams of tetrazo-ditolyl chloride were decomposed by a solution of sodium methylate in methyl alcohol. The sodium methylate was prepared by dissolving 15 grams of clean bright metallic sodium in 250c.c. of absolute methyl alcohol, the alcohol being kept in ice water while the reaction was going on. This solution was used for the decomposition of the diazo-compound. It was put into a flask and cooled by a freezing-mixture. The diazo-compound was added in small portions from time to time, and the mixture well shaken. The action took place energetically. Nitrogen was freely evolved, and a rise in temperature followed each addition of the diazo-compound. For the decomposition of the 20 grams of the diazo-compound about 15 minutes were required. The temperature was kept below 20° . The solution turned red at first, and finally almost black and much tarry matter separated. After the decomposition was over, the methyl alcohol was distilled off, and the contents of the flask subjected to distillation with steam. Drops of an oil were thus carried over which was taken up in ether, dried, and distilled. It was easily recognized as m.ditolyl. This oil is not very volatile with steam, and it is almost impossible

to separate all of it from the tar by this means. The yield of the crude m-ditolyl was five grams.

Action of methyl alcohol on the diazo-compound in the presence of sodium hydroxide.-

20 grams of tetrazo-m-ditolyl chloride were decomposed with 200c.c. of absolute methyl alcohol in which 10 grams of sodium hydroxide had been dissolved. As before, the alcohol was cooled in a freezing-mixture, and the diazo-compound added in small portions. The reaction proceeded exactly as in the preceding experiment, the reaction being very energetic, almost violent, the alcohol warming up, the solution darkening, and tar separating out as before. As soon as the reaction was completed the alcohol was distilled off and the residue distilled in steam. m-ditolyl passed over which was separated from the water with ether. 5 1/2 grams were thus obtained. In both of these experiments as was to be expected from the work of Beeson and that of others in this laboratory the "hydrogen reaction" took place. A diligent search was made for any ether that might have been formed, but ~~such a~~ the search was fruitless.

Action of methyl alcohol on the diazo-compound in the presence of zinc dust.-

10 grams of the diazo-compound was put in a flask

containing 10 grams of zinc powder and 100c.c. of absolute methyl-alcohol. There was no immediate action, though the solution darkened gradually, and, on shaking, a slight evolution of nitrogen was observed, but the decomposition was very slow. After standing for 24 hours most of the diazo-compound remained undecomposed. The flask containing the mixture was then attached to a return-condenser and heated up on a water-bath. The decomposition proceeded smoothly, and, when the reaction was over, the solution was of a light yellow color. This was filtered to remove the zinc dust, and then the methyl-alcohol distilled off. There remained in the distillation-flask a dark red oil which was distilled in steam, separated from the water by ether, and the yield from 10 grams of the diazo-compound was 4 1/2 grams of crude *m*-ditolyl. In this decomposition there was no formation of anything of a tarry nature, and the reaction was perfectly clean. In this as also in the decompositions in the presence of sodium-hydroxide and sodium-methylate a strong odor resembling aldehyde was noticed which was probably paraldehyde. When 10 grams of the diazo-compound were decomposed with ethyl-alcohol in the presence of zinc dust, the decomposition took place in exactly the same manner as when methyl-alcohol was used. At the end of the operation the solution cleared up to a light yellow. The yield of *m*-ditolyl from

the 10 grams of the diazo-compound was 4 grams. It was thought advisable to make quite an amount of the m-ditolyl, and repeat to some extent the experiments of Schultz. 100 grams of tolidine hydrochloride were diazotized, and the diazo-compound precipitated in the usual manner. The diazo-compound was decomposed with methyl alcohol in the presence of zinc dust. The clear yellow resulting solution was filtered from the zinc, and the alcohol distilled off. There remained in the flask a considerable amount of a reddish oil. To the water-alcohol mixture, from which the diazo-compound had been precipitated and which was already of a reddish color, zinc dust was added, the flask attached to a return condenser, and the mixture boiled. The decomposition of the diazo-compound therein remaining was thus effected, and the solution cleared up as in the cases with absolute alcohols to a light yellow. The zinc dust was filtered off, and most of the alcohol removed by distillation, when an oil separated out which was removed with a separating-funnel, and added to that obtained from the decomposition with absolute methyl-alcohol and zinc dust. The oil was then taken up in ether, dried with calcium chloride and distilled from a distillation-flask of appropriate size. 48 grams of m-ditolyl boiling at 279° were then obtained. The yield of the pure substance is thus 76% of the theoretical amount. The real

yield was even greater than this, the operation being attended with considerable loss. After all of the m.ditolyl had distilled off, the thermometer rose rapidly ~~up~~ to 360°above which point a few drops of a strongly smelling oil passed over, but it was obtained in such small amount that no attempts were made to find out what it was. The decomposition of tetrazo-m.ditolyl chloride with the alcohols in the presence of zinc dust furnishes us with a very satisfactory method for the preparation of m.ditolyl. The manipulation is very simple and the yield excellent. Heretofore there have been three methods for its preparation.

(1) Heating zinc powder with o.dicresol,

(2) Converting dichlor-ditolyl to m.ditolyl by sodium amalgam in alcoholic solution, sodium in solution in amylalcohol, or by means of zinc and hydrochloric or acetic acid.

(3) By the action of nitrous acid on an alcoholic solution of o.tolidine. This method was discovered by Schultz and used by him and Stolle in their investigations on m.ditolyl, being the most satisfactory and economical method of the three. The yields of m.ditolyl as given by them is never as much as 25% of the theoretical amount. Several subsequent experiments of mine have shown that a very satisfactory and perhaps the most useful method for the preparation of

m.ditolyl is the decomposition of the tetrazo-*m*.ditolyl-chloride with ordinary 95% alcohol in the presence of zinc dust, the separation of the ditolyl being accomplished as described above. 75% of the theoretical yield of *m*.ditolyl can be very simply and easily obtained in this way. We next turned our attention to the consideration of this substance.

OXIDATION OF *M*.DITOLYL.

According to Schultz and Stolle, when *m*.ditolyl is oxidized with potassium bichromate and sulphuric acid the product is isophthalic acid. I attempted to reach This ~~such~~ ~~a~~ result by using The ~~such~~ proportions ~~as are~~ generally used in such cases, and the acid diluted with two volumes of water. After several hours' boiling the oxidation had taken place only very slightly. It was found that this oxidation is ~~was~~ best effected by using acid diluted to just half its volume with water and about six times the calculated amount of potassium bichromate. The oxidation proceeds smoothly after the first violent reaction is over. After two hours' boiling of the mixture the oxidation is practically completed. After cooling the solid was filtered off, washed with cold water, dissolved in a dilute solution of sodium carbonate ~~solution~~ and the solution of the sodium salt of the acid formed was decolor-

ized with animal charcoal. On the addition of hydrochloric acid, the isophthalic acid was precipitated perfectly white. This was crystallized from water and its melting-point taken. The yield of isophthalic acid is very good by this method. Five grams of *m*-ditolyl were dissolved in glacial acetic acid, and the calculated amount of chromic acid for its total conversion to diphenyldi-*m*-carboxylic acid was added, this also in acetic acid solution. The action was quite violent at first but soon subsided. This solution was then put in a flask attached to a return condenser, and boiled for several hours. Most of the acetic acid was then distilled off and water added, when a slight precipitation of the desired acid resulted, which was filtered, washed with water, purified, and crystallized ~~till~~ until the melting-point became constant. The acid melts at 190.5° ~~C~~. For the oxidation of *m*-ditolyl in repetition of Perrier's work with nitric acid (sp.gr.1.14) four days were necessary, the acid being boiled continually. On cooling a white substance separated which was dissolved in a dilute solution of sodium carbonate ~~solution~~, precipitated with hydrochloric acid, and crystallized from a water-alcohol mixture. It was recognized by its melting-point (202°) as the acid obtained by Perrier. It was thought advisable to try the action of potassium permanganate as an oxidizing agent

on *m*-ditolyl but this powerful reagent was unable seemingly to overcome the resistance of the hydrocarbon to oxidation. A neutral solution of the permanganate was first tried but no oxidation resulted. The potassium permanganate was then tried in potassium hydroxide solutions of many concentrations, but the *m*-ditolyl was never oxidized. This oxidation was attempted at a temperature of the boiling point of water. A slight addition of the permanganate gave the solution a color which hours of heating in contact with the hydrocarbon did not remove. *m*-Ditolyl resists most strongly all oxidizing agents, and the only one ~~in~~ which gave good ~~the~~ results ~~were good~~ was the mixture of potassium bichromate and sulphuric acid which oxidized the hydrocarbon to isophthalic acid.

Action of nitrous acid on tolidine monohydrochloride suspended in alcohol.-

As has been stated Schultz obtained *m*-ditolyl and diethoxy-*m*-ditolyl, by the action of nitrous acid on an alcoholic solution of tolidine. From the work above recorded, it will be seen that we have obtained the same products by decomposing with alcohol the product obtained by the action of nitrous acid on tolidine dihydrochloride. For the sake of completeness it was desirable to know the products

resulting from the decomposition with alcohol of the product formed by the action of nitrous acid on tolidine monohydrochloride. This substance was made by the method of Hugo Schiff and A. Ostrogovich (1) by adding to a hot concentrated solution of the tolidine dihydrochloride a concentrated solution of the calculated amount of sodium acetate, when it is precipitated. The diazotization was first attempted in water suspension in the hopes of getting the diazo-compound by careful diazotization, but only a tarry mass was obtained. When diazotized in alcoholic suspension a red solution was obtained which was boiled with animal charcoal and filtered. On cooling, a small quantity of diethoxy-*m*-ditolyl crystallized out. The alcohol was evaporated and the residue distilled in steam and a few drops of *m*-ditolyl were obtained.

Action of normal propyl alcohol on tetrazo-ditolyl chloride. In order to make the ~~subject~~ investigation more complete, the diazo-compoud was decomposed with propyl alcohol under different conditions. In the first case 13 grams of the diazo-compound were placed in a small flask and 200c.c. of the alcohol added. The flask was attached to a return-condenser and heated in a water-bath in which the water was boiling briskly.

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(1) Ann. Chem. , 278-375.

It was afterwards found best to heat the flask, placed on a wire gauze, with a small flame until the reaction begins. The flame is then removed and the reaction proceeds smoothly the heat generated thereby being nearly sufficient to carry it to completion. A little further heating clears the solution up to a wine color. From the 13 grams of the diazo-compound there was obtained, by distilling off the alcohol and redistilling the residue in steam, more than three grams of m.ditolyl or 40% of the theoretical amount. Other experiments proved that the yield of m.ditolyl by this method was at least 45% of the theoretical amount. 11 grams of the diazo-compound were decomposed in exactly the same manner except that ten grams of zinc powder was added. The decomposition was rather more energetic than before, the solution clearing up at the end of the operation to an amber color. On filtering off the zinc dust and evaporating the alcohol, a dark colored oil was left and, as in all cases in which I had used zinc dust before, there was a total absence of the formation of any tarry products. The oil remaining was taken up in ether, dried with calcium chloride and distilled. A little less than four grams was thus obtained of m.ditolyl or a yield of at least 60% of the theoretical amount.

The addition of sodium hydroxide to propyl alcohol used in the decomposition of the diazo-compound caused the

decomposition to take place at room temperature very rapidly. Tarry products were formed in abundance and the reaction that took place was the "hydrogen" one, though the yield was not good. In none of the decompositions with propyl alcohol did the "alkoxy" reaction take place at all for all efforts to separate any phenol-ether were of no avail. The "hydrogen" reaction takes place and that alone when tetrazoditolyl chloride is decomposed with propyl alcohol.

B. - Tetrazo-diphenyl Chloride.

Preparation of benzidine hydrochloride -

100 grams of benzidine were mixed with 600c.c. of water in a large evaporating dish, and the mixture heated almost to the boiling point of the water. Hydrochloric acid was now added in slight excess and all the benzidine went into a red solution. To this red solution animal charcoal was added, and the solution was boiled for a few minutes and filtered hot, when a perfectly colorless solution resulted. To this was added one-fourth of its volume of strong hydrochloric acid gradually with stirring, when the benzidine hydrochloride was precipitated as a very finely crystalline mass perfectly white. The hydrochloride obtained by this

method is almost perfectly pure as the hydrochlorides of the isomeric benzidines remain in solution. This was filtered off as dry as possible with the aid of a Büchner funnel and filter pump, and was then, while still slightly moist, bottled, and used in that condition, as the quality of the diazo-compound was found to be much better when a little hydrochloric acid was still present. This salt when allowed to stand in the air gradually becomes coated with a covering of a purplish color.

Preparation of tetrazodiphenyl chloride.-

Several methods were tried for the purpose of getting this compound in best condition and yield, and the one finally adopted which gave the best results I will describe. As in the diazotiation of tolidine hydrochloride a paste of the hydrochloride and water was used. In this instance it was found more necessary to keep the paste of benzidine hydrochloride and water at a low temperature than was found necessary in the case of tolidine hydrochloride. To accomplish this the oxides of nitrogen formed in the usual manner were passed through a Wolff's bottle which was surrounded with salt and ice, and then the cooled gases were led into a cylinder which contained the paste of the benzidine hydrochloride and water, and was surrounded with ice.

In order to diazotize the hydrochloride completely, about three parts of water are necessary to one of the salt. For the precipitation of the diazo-compound six times the volume of the water solution of the diazo-compound of ordinary alcohol is required. This is previously cooled to as low a temperature as a freezing mixture can cool it, and passed into the solution of the diazo-compound. A precipitation of the diazo-compound in the form of beautiful needles at once takes place. The vessel containing this mixture is then allowed to stand in the freezing-mixture for some time and the diazo-compound filtered off. If the diazotization has resulted happily, and the water solution is of a light straw-color, as it should be, the crystals of tetrazo-diphenyl-chloride are almost perfectly white. Unfortunately, even if one works with the greatest care, this state of affairs is not reached every time. But, if attention is paid especially towards keeping the temperature of the paste which is being diazotized below 5°, and the alcohol for precipitation is cold, a good quality of diazo compound will be obtained. The diazotization is best effected by means of a rapid current of the oxides of nitrogen and indeed this is necessary for a successful diazotization which is best effected in from 20 to 25 minutes. My early attempts at making this diazo-com-

pound were failures because the current of gases was too slow, and the diazotization occupied too long a time. Tetrazo-diphenyl-chloride is a rather heavy substance, settling rapidly to the bottom of the beaker in which it is precipitated. When filtered, washed with alcohol and ether and dried, it can be handled safely although it is not as stable a compound as is tetrazo-ditolyl-chloride. The yield of the diazo-compound by this method is about 85% of the theoretical amount. The change in color during diazotization is not as marked as in the case of the diazotization of tolidine-hydrochloride. When the gases are first passed into the mixture, a slight brown discoloration takes place, which continues until near the end of the operation, when a clearing up to a light yellow takes place, when the diazotization proceeds best. Otherwise a reddish discoloration takes place which is of a tarry nature and which never disappears. The greatest care is necessary in keeping the alcohol and water solution of the diazo-compound cold before they are brought together for the precipitation of the diazo-compound, as it is also necessary to keep the mixture cold afterwards. If This ~~such~~ is not done when the two are brought together, a decomposition will begin, which colors the solution ~~a~~ dark red and makes the diazo-compound precipita~~ted~~ formed very impure. An important point of difference between tetrazo-ditolyl-chloride

and tetrazo-diphenyl-chloride is the fact that the latter is easily decomposed at room temperature (especially in alcohol largely diluted with water) in which case tarry products are principally formed . If the same decomposition is effected at the boiling point of the mixture, the reaction is much cleaner.

Action of methyl-alcohol on tetrazo-diphenyl-chloride.-

20 grams of the diazo-compound were placed in a 2-liter flask and 300c.c. of absolute methyl-alcohol poured over the diazo-compound. If this mixture is allowed to stand there will be a gradual darkening, and slow decomposition will ensue, but the action will be incomplete, and the results very unsatisfactory. The amount of tarry matter formed will be much larger than if the decomposition is carried on at a higher temperature. When the flask containing the mixture of the diazo-compound and alcohol is attached to a return condenser and heated over a water-bath, the reaction is very satisfactory provided certain precautions are observed. There will be little evolution of nitrogen until the boiling point of the alcohol is almost reached. As soon as the evolution of nitrogen begins, the flame is removed from under the water-bath and the action quickened by shaking the contents of the flask. The reaction proceeds smoothly. When the evolution of nitrogen almost ceases, the mixture

is heated to boiling for fifteen minutes to complete the reaction. The solution resulting is of a light reddish color, and the reaction seems to have been quite clean. The methyl# alcohol is then distilled off and six volumes of a saturated solution of sodium#chloride added, when a faint milkiness results. On standing, there settles to the bottom of the vessel a slight precipitate which ~~is~~ was afterwards proved to be diphenyl. After distillation of the methyl#alcohol there remains in the flask a yellow solid which seems to contain very little matter of a tarry nature. This is broken up, a little water added, and distillation in steam carried on, when a small inappreciable amount of a white solid is carried over by the steam which melts at 68 ° and by ~~this~~ the [illegible] and its odor is recognized as diphenyl. The yellow solid remaining in the flask which is not volatile with water vapor is then dissolved in ordinary alcohol, in which it is difficultly soluble at its boiling temperature, and almost insoluble in the cold. As in the case of the two phenol-ethers which have already been described, this substance showed a marked difference in its solubility in alcohol at its boiling temperature and a few degrees below that temperature. The alcoholic solution was then decolorized by boiling with animal charcoal for a few minutes and on cooling, beautiful plates of a pearly lustre were obtained. In this first experiment

the yield was 8 grams. When the substance was a second time crystallized from alcohol the melting-point was sharp at 172°. All of the properties of this substance were those of the ethers which have been described in the preceding pages and although it was probable that it was an ether yet an analysis was desirable. Two analyses gave the following results:

(1) 0.2000 gram substance gave 0.1193 gram H_2O and 0.5775 gram CO_2.

(2) 0.2000 gram substance gave 0.1181 gram H_2O and 0.5751 gram CO_2.

The calculated percentage of the elements in dimethoxy-diphenyl, $C_{12}H_8(OCH_3)_2$ one C -78.50, H - 6.54 and 0-1496

	calculated.	found. (1)	(2)
C -	78.50	78.75	78.43
H -	6.54	6.62	6.56
O -	14.96	14.63	15.01

The yield of diphenyl by the action of methyl alcohol on tetrazo-diphenyl chloride is very small, and may be left out of consideration, and we can say that, when these bodies are brought together, the reaction that takes place is the "alkoxy". The reaction resulting in the formation of the phenol ether is almost a quantitative one although the losses in

extraction always bring the actual yield far below the amount theoretically possible. The largest yields obtained range from 65% to 70% of the theoretical amount. Dimethoxydiphenyl is insoluble in water, difficultly soluble in alcohol, and ether. In alcohol it is not as soluble as are dimeth - and diethoxy-m.ditolyl. When this decomposition is effected with dilute methyl alcohol, it takes place more readily, and the products are the same, but the phenol-ether is formed in smaller amount, and a considerable amount of products of a tarry nature are formed at the same time, being relatively greater in amount the greater the dilution of the alcohol.

Decomposition of tetrazodiphenyl chloride with methyl alcohol under different conditions.-

16 grams of the diazo-compound were put in a flask of appropriate size and 250c.c. of methyl alcohol added. 15 grams of zinc dust were now added and the diazo-compound decomposed in the usual way. The decomposition did not begin until the alcohol was almost at its boiling temperature, and then proceeded smoothly as in the preceding experiment. The flame was removed as soon as the reaction began and the heat generated thereby was sufficient to carry it almost to completion. In order to be perfectly sure that the reaction

was complete, the solution was heated to the boiling-point of the alcohol for a few minutes. The yellow resulting solution was now filtered to remove the zinc dust, and the alcohol distilled off. A portion of the distillate was treated with 6 volumes of a saturated solution of sodium chloride, and a slight precipitation resulted. After this the alcohol was not precipitated, but saved for use in other decompositions, as the phenol-ether is not volatile with alcohol vapor and diphenyl is so only to a slight degree. There was left in the flask as before a yellow solid which was now subjected to distillation in steam. As was to be expected most of it was carried over as a white solid with the water vapor which when crystallized from alcohol melted at 68° and was easily recognized by its odor and general properties as diphenyl. There was obtained in this experiment a yield of 6 1/2 grams of the substance which is 73% of the theoretical yield. ~~(Before this time in an experiment to be described later diphenyl had been analysed, hence my easy recognition of it).~~ The brownish residue in the distillation flask was dissolved in alcohol and carefully examined for dimethoxydiphenyl, but the search only revealed the fact that none was formed in the reaction. ~~All~~ During the decomposition a strong odor was noticeable resembling that aldehyde,

which was perhaps paraldehyde as the work of Reesen showed. As in all other decompositions recorded here which were carried on in the presence of zinc dust the reaction is practically clean, and the presence of the zinc dust determines the hydrogen reaction. Decompositions of tetrazo-diphenyl chloride with sodium methylate, and with methyl alcohol in the presence of sodium hydroxide, were also tried, but only small amounts of the diazo-compound were thus decomposed, the object simply being to find out which way the reaction went. The decompositions proceeded in ~~an~~ exactly ~~similar~~ the same way in both cases. The flasks containing the two mixtures were cooled in a freezing-mixture, and the diazo-compound added in small portions from time to time. The reaction after each addition was violent, heat being generated and much tarry matter formed. The yields were not determined, but in both cases diphenyl was formed which was separated by distillation in steam. No dimethoxy-diphenyl was formed. The hydrogen reaction takes place when tetrazo-diphenyl chloride is decomposed with methyl alcohol in the presence of zinc dust, sodium hydroxide or sodium methylate.

Action of nitric acid or dimethoxy-diphenyl -

Small quantities of the phenol-ether were treated with dilute, concentrated, and fuming nitric acid. Dilute

nitric acid attacks it not at all even when boiled. Concentrated nitric acid slowly dissolves the ether when the acid is heated to its boiling temperature, but it requires quite a length of time and much of the ether is oxidized. When water is then added there is very little precipitation of a nitro-compound. The best yield was obtained by the employment of fuming nitric acid, the nitration being effected exactly as in the case of diethoxy-m-ditolyl. 5 grams of dimethoxy-diphenyl were placed in a large test-tube, and fuming nitric acid added until the phenol-ether went into solution. The action is rather violent, much heat being generated, and the oxides of nitrogen escaping. The resulting solution is of a deep red color. After the violence of the reaction has subsided, the solution is heated for a few moments almost to the boiling-point of the acid, and then poured with stirring into a large volume of water, when a voluminous precipitate of a light yellow color is thrown down. This is filtered off and dried. Thus were obtained of the crude nitro-compound 4 1/2 grams. This is insoluble in water, in cold alcohol, and ether, and very sparingly soluble in boiling alcohol. With a liter and a half of ordinary alcohol ten extractions were necessary before all of the substance had gone into solution. A hot-water funnel was necessary in filtering the alcoholic solution, as the nitro-

compound was only soluble in alcohol at its boiling temperature. It crystallizes from alcohol in beautiful straw yellow needles which melt sharply at 244.6°. Three analyses for nitrogen gave as the percentage of that element in the substance 14.6, 14.1 and 14.5, which agree well with the formula $C_{14}H_{10}O_2(NO_2)_4$ for which the percentage of nitrogen is 14.22.

Action of tetrazodiphenylchloride on ethyl alcohol.-

23 grams of tetrazodiphenylchloride were placed in a two-liter flask and 300c.c. of absolute ethyl alcohol poured over it. The flask was then attached to a reflux condenser and heated on a water-bath. The heating of this mixture for the decomposition of the diazo-compound requires the greatest care and special precautions must be taken. Near at hand a water-bath containing cold water is placed. The mixture is well shaken while the heating is going on and carefully watched. The reaction does not begin until the boiling temperature of the alcohol is almost reached. As soon as evidences of decomposition are observed, the flame is removed, the water-bath containing hot water is taken away, and the one containing cold water gotten in readiness. The mixture is now shaken and the decomposition begins. When it increases in violence, the flask is plunged in the cold water

until it partially subsides, and then removed. These operations are repeated until the reaction is over and all the diazo-compound has gone into a reddish-yellow solution. This is then heated and the alcohol boiled for a few moments to insure complete decomposition. Throughout the operation the strong odor of aldehyde is observable through the entire room, and it is evident that the reaction that took place was to a large extent the "hydrogen" one. The first decomposition of tetrazo-diphenyl chloride with ethyl alcohol was carried on in the same manner as were those with methyl alcohol, and the violence of the reaction was so great that the greater part of the reacting mixture was projected through the condenser tube across the room. In several subsequent experiments where special precautions were not observed a considerable loss was occasioned by the same violence. The method described above is that by which the best results were obtained. In the experiment described the reddish solution of the decomposition-products was subjected to distillation and all of the alcohol removed in this way. There remained in the flask a reddish oil which, on cooling, solidified to a reddish crystalline solid. The alcoholic distillate was tested by adding to it several volumes of a saturated solution of sodium chloride, and a slight precipitation

of a white solid resulted. The rest of the alcohol was not treated in the same way because the substance was only slightly volatile with alcohol vapor but was preserved for further decompositions. The reddish residue in the distillation flask was distilled in steam, and most of it passed over with the water vapor as a white crystalline solid having the strong odor of diphenyl, and melting when crystallized from alcohol at 68°. The yield was 10 1/4 grams or over 80% of that theoretically possible. The small amount of the red solid remaining in the flask was filtered off, and dissolved in alcohol, but not a trace of any phenol-ether was ever obtained from it. The indications were strongly in favor of this white solid, volatile with water vapor, being diphenyl, but an analysis was made of it for the sake of certainty ~~to become perfectly certain because~~ If ~~such~~ this is the case this method of preparation would be a very valuable addition to those that we have already, because of the easily obtained benzidine, the ease of its transformation to diphenyl and the large yield.

(1) 0.2000 gram substance gave 0.1179 gram H_2O and 0.6841 gram CO_2.

(2) 0.2000 gram substance have 0.1171 gram H_2O and 0.6925 gram CO_2.

For diphenyl the percentages of carbon and hydrogen

are respectively 93.51% and 6.49%

	calculated	found (1)	found (2)
C -	93.51	93.30	93.07
H -	6.49	6.55	6.50

Thus we see that the substance formed by the action of tetrazo-diphenyl-chloride on ethyl-alcohol is diphenyl and that the "hydrogen reaction" alone takes place in this case.

Diphenyl was discovered in 1862 by Fittig (1) by means of the reaction that has come down to us under his name. He made it by the action of sodium on brom-benzene which had been diluted to half its volume with ether. In 1864 Griess (2) by the action of an alcoholic solution of potassium hydroxide on diazo-benzene-nitrate obtained besides benzene a crystalline solid which by comparison with a specimen of diphenyl obtained from Fittig he recognized as identical with it. The method by which this substance is commonly made in the laboratory was devised by Berthelot, (3) and consists in passing benzene vapor through a red hot tube filled with broken glass. This method is not easy of manipulation, and is attended with not a little danger to an inexperienced worker. Gatterman (4) devised the method of making

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(1) Ann. Chem. ., 121-361.
(2) Phil.Tr., 1864- (3) 692.
(3) Ann.Chem.142-252. Zeit.f.Chem. 1866-707.
(4) Ber.d. Chem. Ges. 23-1226.

diphenyl by the action of zinc dust on diazo-benzene-sulphate and alcohol.

Decomposition of tetrazo-diphenyl-chloride with ethyl-alcohol under various conditions.-

Knowing that in all cases in which zinc powder was used in this investigation the "hydrogen reaction" was facilitated by its employment, it was thought that the method described above for the preparation of diphenyl might be improved by its use. As in the decompositions described extreme care was necessary to prevent the reaction from taking place with too much violence. Decompositions were carried on with absolute alcohol, ordinary 95% alcohol and alcohol still more dilute in the presence of zinc dust which was added in about the same amount as the diazo-compound. It was found that, as long as the alcohol did not contain over 15% of water, ~~that~~ the decompositions proceeded similarly to those with absolute alcohol. Under proper conditions the reaction was smooth and the decomposition perfectly clean, no tarry products being formed and the solution clearing up at the end of the operation to a straw yellow. The zinc powder was now removed by filtration and the yellow resulting solution decolorized with animal charcoal and evaporated until crystallization took place. Diphenyl was thus obtained

perfectly pure by recrystallizing this product from alcohol. The yield ~~from~~ this method is from 80% to 85% of the theoretical amount. When the alcohol contains more water than 15%, tarry products are formed, their amounts being greater the greater the dilution of the alcohol, and the amount of diphenyl relatively smaller. In this connection it is well to repeat what I have mentioned when speaking of the precipitation of the diazo-compound. The alcohol-water mixture which precipitated the diazo-compound and which contains over 20% of water must be kept very cold, for decomposition sets up rapidly if it is taken from the freezing-mixture, with the formation of some diphenyl and a large amount of tarry products.

Sodium-hydroxide added to the ethyl-alcohol used for the decomposition of tetrazo-diphenyl-chloride causes a violent reaction to take place at room temperature, and a freezing-mixture is required to keep the decomposition within bounds. A large amount of tarry products is formed and diphenyl is separated by distillation of the alcohol, and distilling the residue in steam. For a laboratory method for the preparation of diphenyl I would suggest the decomposition of tetrazo-diphenyl-chloride with ordinary alcohol in the presence of an excess of zinc powder. In all cases in which tetrazo-diphenyl-chloride was decomposed with ethyl

alcohol diphenyl was formed, and no trace of diethoxy-diphenyl was ever obtained, and we are justified, I think, in saying that when these two substances react the "hydrogen" reaction and only that takes place.

Action of normal propyl-alcohol on tetrazo-diphenyl-chloride.

12 grams of tetrazo-diphenyl-chloride were placed in a half-liter flask and 150c.c. of propyl-alcohol added. At room temperature there was practically no action at all, although when the mixture was allowed to stand for several hours the alcohol became colored reddish. The flask was attached to a reflux condenser and the alcohol heated to its boiling temperature with a small flame. As soon as the decomposition begins, the flame is removed, and the decomposition allowed to proceed. The heat generated by the reaction is almost sufficient to carry it to completion. The alcohol was then boiled for a few minutes and the alcohol distilled off. There remained a brownish residue which was subjected to steam distillation. A little over three grams of diphenyl were obtained. This experiment repeated several times showed that the yield of diphenyl by this method was between 40% and 50% of the theoretical yield. When the steam distillation was completed there remained in the flask some tarry matter from which nothing of value was obtainable.

When the diazo-compound is decomposed with propyl-alcohol in the presence of an excess of zinc dust the reaction takes place in the same manner, but is much cleaner and the amount of tarry products is reduced. By this method the yield of diphenyl can be brought up to 60% of the theoretical amount. The addition of sodium hydroxide to propyl-alcohol used for this decomposition causes the reaction to take place at room temperature and diphenyl is formed together with much matter of a tarry nature. As was found in case of the decomposition of tetrazo-ditolyl-chloride with propyl-alcohol so, in case of the decomposition of tetrazo-diphenyl-chloride with the same alcohol the "hydrogen" reaction alone takes place.

Summary of experimental work.-

Tetrazo-ditolyl-chloride when decomposed with methyl-alcohol yields as the only ~~isolatable~~ product dimethoxy-*m*.ditolyl or the "alkoxy" reaction alone takes place.

$$C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{12}(OCH_3)_2 + 2N_2 + 2HCl.$$

When the same diazo-compound is decomposed with ethyl-alcohol the products of the reaction are *m*.ditolyl and diethoxy-*m*.ditolyl in approximately equal quantities or both the "hydrogen" and "alkoxy" reactions take place.

$C_{14}H_{12}N_4Cl_2 + 2C_2H_5OH - C_{14}H_{14} + 2C_2H_4O + 2N_2 + 2HCl$

$C_{14}H_{12}N_4Cl_2 + 2C_2H_5OH - C_{14}H_{12}(OC_2H_5)_2 + 2N_2 + 2HCl$

When the same diazo-compound is decomposed with normal propyl alcohol the only product isolated was m.ditolyl or the "hydrogen" reaction alone takes place:

$C_{14}H_{12}N_4Cl_2 + 2C_3H_7OH \;)\; C_{14}H_{14} + 2C_3H_6O + 2N_2 + 2HCl$

When the same diazo-compound was decomposed with a solution of sodium methylate in methyl alcohol the "hydrogen" reaction alone took place. The same reaction took place when the diazo-compound was decomposed with each alcohol in turn in the presence of sodium hydroxide or zinc powder. When tetrazo-diphenyl chloride is decomposed with methyl alcohol, the product is dimethoxy-diphenyl and, at the same time, a trace of diphenyl is formed, the "alkoxy" reaction taking place almost exclusively:

$C_{12}H_8N_4Cl_2 + 2CH_3OH = C_{12}H_8(OCH_3)_2 + 2N_2 + 2HCl.$

The decomposition of the same diazo-compound with ethyl alcohol gives only diphenyl or the "hydrogen" reaction alone takes place:

$C_{12}H_8N_4Cl_2 + 2C_2H_5OH = C_{12}H_{10} + 2C_2H_4O + 2N_2 + 2HCl$

The same diazo-compound decomposed with normal propyl alcohol yields only diphenyl or the "hydrogen" product:

$C_{12}H_8N_4Cl_2 + 2C_3H_7OH = C_{12}H_{10} + 2C_3H_6O + 2N_2 + 2HCl.$

Sodium methylate in methyl alcohol solution yields in the

decomposition of the diazo-compound therewith only diphenyl. When the diazo-compound is decomposed with either methyl, ethyl, or propyl alcohol in the presence of sodium hydroxide or zinc powder the "hydrogen" reaction alone takes place.

- Notes -

The tolidine used in this ~~experiment~~ investigation was commercial *o*.tolidine which, when purified, melted at 126.5°. It was purified by conversion into the hydrochloride, decolorizing its solution with animal charcoal, and precipitating the tolidine with potassium hydroxide. Tolidine crystallizes from water in beautiful pearly leaves.

The benzidine used was commercial *p*.benzidine which was purified in the same manner as was the tolidine. It crystallizes from water in pearly leaves, melting at 120.5°.

The methyl alcohol used was commercial "Columbian spirits" which was allowed to stand in contact with lime for some weeks and then distilled. It was preserved by keeping it in tightly-stoppered bottles over dehydrated cupric sulphate, and was poured off and distilled as needed.

The ethyl alcohol was allowed to stand in contact with lime for several weeks and then was distilled. It was then kept in contact with dehydrated cupric sulphate from

which it was filtered as needed.

The propyl-alcohol was normal propyl-alcohol which was treated with lime in a flask attached to a return condenser for several hours and then distilled.

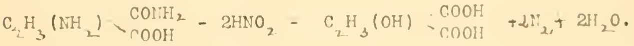
The term "ordinary alcohol" used is to designate the commercial article which contains about 95% of alcohol.

The temperatures here given are all uncorrected.

More correctly, as has been shown lately, the derivations of the tolidine and benzidine that I have worked with are "diazonium-compounds" but throughout this investigation the old nomenclature is used.

II. - - HISTORICAL AND GENERAL PART.

Our earliest knowledge of the interesting action of nitrous acid on amido-compounds comes from the labors of Piria (1) who found that asparagine in nitric acid solution was converted by nitrous acid to malic acid according to the equation,



$$C_2H_3(NH_2)\begin{matrix}CONH_2\\COOH\end{matrix} - 2HNO_2 - C_2H_3(OH)\begin{matrix}COOH\\COOH\end{matrix} + 2N_2 + 2H_2O.$$

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(1) Ann. Chem. 68-349.

About the same time, in 1849, Strecker (1) obtained glycolic acid by the action of nitrous acid on amido-acetic acid. The same kind of reaction was also observed in amido-compounds belonging to the aromatic series. Hunt, in 1849, proved that nitrous acid converted aniline to phenol, and Gerland, in 1853, prepared in a similar manner oxybenzoic acid from amido-benzoic acid. But it was not until 1856 that a product was obtained by the action of nitrous acid which had more nitrogen than the original substance. It was in that year that Ganahl (2) obtained such a substance by the action of nitrous acid on naphthylamine. Then came the master-workman Griess (3), whose researches in this field are mentioned among the classics in chemistry. It is of the work of Griess that one always thinks when diazo-compounds are mentioned. He showed that, when the aromatic amido-compounds are treated with nitrous acid, no nitrogen is evolved under certain circumstances, and that, by a reaction between the two, a compound results which contains the nitrogen of the nitrous acid as well as that of the amido group. He called the resulting compound a "diazo-compound" from the number of nitrogen atoms which it contained. Among many reactions of these compounds described by him was that one with the alcohols.

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(1) Ann. Chem. 68-54.
(2) Ann. Chem. 99-240.
(3) Ann. Chem. 137-68.

He, from the results of much work and many experiments in this field, made the general statement that when a diazo salt is boiled with an absolute alcohol the hydrocarbon corresponding to the diazo-compound is formed, the alcohol is oxidized to the aldehyde and nitrogen is evolved. His work on diazo-compounds beginning in 1860 extended over a period of a number of years. In 1870, Wroblewsky,(1) while attempting to replace the amido groups in the isomeric chlortoluidines by hydrogen by boiling the diazo derivatives with alcohol according to the method of Griess found that instead of hydrogen replacing the amido groups they were replaced by the "alkoxy" residue of the alcohol. ~~This at once gave an impetus to work in this field and many workers attacked the problem.~~ For the last fifteen years investigations have been carried on in this laboratory on the decomposition of diazo-compounds with alcohols and many results of value have been reached. I think that I am justified in drawing the following conclusions from the results which have been obtained in the investigation which has been described. -

(1) That Graham's conclusion "All diazo-compounds having more than one benzene ring give the 'hydrogen' reaction" is subject to limitations for both of the diazo-compounds studied which fall under this head under certain circumstances

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(1) Ber. d. Chem. Ges. 3-98.

give only the "alkoxy" reaction.

(2) Metcalf's suggestion that the nature of the alcohol may affect the reaction has been confirmed to a marked degree. Take as an example tetrazo-ditolyl chloride and decompose with methyl, ethyl, and propyl alcohol at the boiling points of the alcohols. With the first, the "alkoxy" reaction takes place only, with the second both reactions result, and with the third only the hydrogen product can be isolated.

(3) This investigation sheds no light on the problem as to whether water in small quantities favors the "alkoxy" reaction or not. In those cases in which the "hydrogen" reaction took place the addition of water did not affect the reaction. In the other cases the addition of water up to 15% neither increased nor diminished the yield of the "alkoxy" product.

(4) The fact that for complete decomposition it was necessary to heat the mixture of the diazo-compound and alcohol made it impossible to study the effect of temperature on the reaction.

(5) The decompositions of tetrazo-ditolyl chloride and tetrazo-diphenyl chloride with a methyl alcohol solution of sodium methylate gave only the "hydrogen" product - a confir-

firmation of the conclusion first put forward by Beeson that a diazo-compound decomposed with this mixture gave the "hydrogen" reaction.

(6) Beeson also states that the presence of sodium hydroxide or zinc dust determined the "hydrogen" reaction. This was also confirmed, and, moreover, in those cases in which that reaction would take place otherwise, the yields were increased by their addition. Especially is this the case with the addition of zinc dust in which case the yields are almost quantitative.

(7) The method described for the preparation of m-ditolyl is simple, easily carried out, and gives 75% of the theoretical yield.

(8) The method described for the preparation of diphenyl is well suited for a laboratory method, being quickly carried out, not dangerous and giving almost theoretical yields.

~~In conclusion let me add that one need feel not the slightest fear in working with these diazo-compounds for they do damage only under the greatest provocation such as would make any self-respecting chemical individual rebel.~~

Biographical

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The author of this dissertation, James Henry Curry Winston, was born in Farmville, Virginia, March 30, 1876. He received his early training in the public schools of his native town, and continued attending them until he was graduated from the High School in 1890. In 1891 he entered Hampden-Sidney College and graduated therefrom in 1894 with the degrees of Bachelor of Arts and Bachelor of Science. Advanced courses of study were pursued by him, 1894-5, at the University of Virginia in the natural sciences and modern languages. The next year was spent in teaching in Tazewell College. In the fall of 1896 he entered the Johns Hopkins University, choosing Chemistry as his principal subject, with Physics and Mathematics as subordinates. On entrance he held an ordinary Virginia scholarship, and, during the other two years of his work here, he has held honorary Virginia scholarships. The time since last October has been spent upon the investigation which forms the basis of this dissertation.